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Date of mailing (day/month/year) 16 August 2000 (16.08.00)	
International application No. PCT/NL99/00776	Applicant's or agent's file reference BO 42290
International filing date (day/month/year) 16 December 1999 (16.12.99)	Priority date (day/month/year) 16 December 1998 (16.12.98)
Applicant THORNTON, Jeffrey, Wilson et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

13 July 2000 (13.07.00)



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Date of mailing (day month year) 28 August 2001 (28.08.01)	
International application No. PCT/SE99/02297	Applicant's or agent's file reference 103372401
International filing date (day month year) 08 December 1999 (08.12.99)	Priority date (day month year) 18 December 1998 (18.12.98)
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1. The designated Office is hereby notified of its election made:

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23 August 2000 (23.08.00)

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NOTIFICATION OF THE RECORDING
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To:

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Date of mailing (day/month/year) 12 June 2001 (12.06.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference BO 42290	
International application No. PCT/NL99/00776	International filing date (day/month/year) 16 December 1999 (16.12.99)

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<input checked="" type="checkbox"/> the applicant	<input checked="" type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A61L 15/60, 15/28	A1	(11) International Publication Number: WO 00/35504 (43) International Publication Date: 22 June 2000 (22.06.00)
(21) International Application Number: PCT/NL99/00776 (22) International Filing Date: 16 December 1999 (16.12.99) (30) Priority Data: 98204273.1 16 December 1998 (16.12.98) EP 99201286.4 23 April 1999 (23.04.99) EP 99201915.8 15 June 1999 (15.06.99) EP (71) Applicant (for all designated States except US): SCA HYGIENE PRODUCTS ZEIST B.V. [NL/NL]; P.O. Box 360, NL-3700 AJ Zeist (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): THORNTON, Jeffrey, Wilson [US/NL]; Jagersweg 13, NL-1272 AC Huizen (NL). SCHRAVEN, Bas [NL/NL]; Zwaluwstraat 128, NL-6541 NR Nijmegen (NL). THIEWES, Harm, Jan [NL/NL]; Nico Bergsteynweg 147, NL-3931 CC Woudenberg (NL). VAN BRUSSEL-VERRAEST, Dorine, Lisa [BE/NL]; Kopeind 1, NL-2411 WG Bodegraven (NL). BEMPORAD, Luca [IT/SE]; Torggatan 12 Apt. 348, S-411 57 Gothenburg (SE). VERWILLIGEN, Anne-Mike [NL/NL]; Oude Armhemseweg 234, NL-3705 BJ Zeist (NL). BESEMER, Arie [NL/NL]; Burg. Jhr. H. v.d. Boschstraat 111, NL-3958		CE Amerongen (NL). KALENTUIN, Pia [SE/SE]; Stora Pölsanväg 7A, S-423 40 Torslanda (SE). (74) Agents: DE BRUIJN, Leendert, C. et al.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL). (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ACIDIC SUPERABSORBENT POLYSACCHARIDES		
(57) Abstract <p>A process is disclosed for producing an acidic superabsorbent polysaccharide derivative, comprising the steps of: (a) crosslinking at least one polysaccharide containing acidic groups, such as carboxymethyl cellulose and/or 6-carboxy starch, with a crosslinking agent to produce a gel; (b) if necessary, adjusting the pH of the polysaccharide to a value between 3.5 and 5.5; (c) comminuting the acidified polysaccharide gel; and (d) drying the comminuted polysaccharide at elevated temperature. The superabsorbent polysaccharide obtainable by this process has a pH below 5 and provides odour control when contacted with malodorous fluids.</p>		

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Acidic superabsorbent polysaccharides

[0001] The present invention relates to a superabsorbent material which has enhanced odour control and prevents bacterial growth, based on polysaccharides, and to a method of producing such material.

[0002] Superabsorbent materials of various types are known in the art. Examples are crosslinked polyacrylates and polysaccharides grafted with polyacrylates. A problem related to the use of superabsorbent materials is the odour caused by urine components which cause superabsorbent materials to become objectionable long before their maximum absorbing capacity has been used. Furthermore, the known absorbent materials are normally based on non-renewable and/or non-biodegradable raw materials. Consequently, there is a need for superabsorbent materials, which have odour control and reduced bacterial growth when contacted with body fluids, and which are biodegradable.

[0003] WO 98/27117 discloses a superabsorbent polysaccharide derivative obtained by oxidation and crosslinking of a polysaccharide such as starch, in which at least 0.1 carbinol group per monosaccharide unit of the polysaccharide derivative has been oxidised to a carboxyl group, the total number of carboxyl groups per monosaccharide unit being 0.2-3.0, and the derivative results from reaction with at least 0.001 equivalent of crosslinking agent per monosaccharide unit. The derivatives are not devised for odour control. US 5,247,072 describes superabsorbent carboxyalkyl polysaccharides, especially carboxymethyl cellulose, without odour control, obtained by crosslinking as a result of heat treatment. EP-A-202127 discloses superabsorbent articles for reducing diaper rash, which contain acid in distinct zones to control the skin pH between 3.0 and 5.5.

[0004] It has been found that a superabsorbent polymer with improved odour control can be produced by a process comprising the steps of:

- (a) crosslinking at least one polysaccharide containing acidic groups with a crosslinking agent to produce a gel;
- (b) ensuring that pH of the polysaccharide is between 3.5 and 5.5 and, if necessary, adjusting the pH to between 3.5 and 5.5, especially to between 3.9 and 4.9;
- (c) comminuting the acidified polysaccharide gel; and
- (d) drying the comminuted polysaccharide at elevated temperature.

[0005] The term "polysaccharide containing acidic groups" is understood to comprise polysaccharides having a pK of less than 5, down to about 1.5. Such polysaccharides may

contain carboxylic groups, sulphonic groups $(-(O)-SO_2-OH)$, phosphonic groups $(-(O)-PO(OH)_2)$, ammonium groups $(-NR_2H^+)$, wherein R is alkyl or hydrogen) and combinations thereof. The carboxylic groups may be present as a result of carboxyalkylation, in particular carboxymethylation, or as a result of reaction with an anhydride such as maleic or succinic anhydride or as a result of oxidation, e.g. of a hydroxymethyl group $(-CH_2OH)$, usually at C6 of a monosaccharide unit), or of a bis(hydroxymethylene) group $(-CHOH-CHOH-)$, usually at C2-C3 of a monosaccharide unit).

[0006] The phosphonic groups may be present as phosphate groups, resulting e.g. from reaction with phosphorylating agents (see e.g. WO 97/28298), or as phosphonic or phosphinic acid groups, resulting e.g. from reaction with halomethyl phosphonic acids. The sulphonic acids may be present e.g. as sulphate groups or as a result of sulphite addition to polysaccharide aldehydes (see e.g. WO 99/29354) or to maleic anhydride adducts (products with $-O-CO-CH-CH(COOH)-SO_3H$ groups). The ammonium groups are also acidic groups, and can result from protonation of amine groups, such as in chitosan-type polysaccharides or in aminoalkylated polysaccharides.

[0007] The polysaccharides may be α -glucans like starch, amylose and amylopectin, β -glucans like cellulose and chitin and scleroglucan, galactomannans like guar gum (guaran) and locust bean gum, glucomannans including e.g. xanthan gum, fructans, (arabino)xylans, galactans including alginates and pectin and other mixed polysaccharides. Starch and cellulose are particularly preferred. Starch may be derived from any suitable source, such as corn, wheat, potato, rice and the like; it may also be a residual, crude or lower-grade starch product containing minor amounts of other biopolymers such as cellulose, pectin or protein. Cellulose may also contain minor amounts of other materials such as hemicellulose.

[0008] The polysaccharides may comprise non-ionic, non-carboxylated derivatives such as hydroxyalkyl polysaccharides, but the presence of such non-ionic derivatives does not have a particular advantage. The chain length of the polysaccharides is important although there is no critical minimum for the molecular weight. In general, polysaccharides having a molecular weight of more than 1,000 are preferred. A molecular weight above about 25,000 may have a positive effect on the properties of the oxidised product.

[0009] The acidic polysaccharide can be a carboxymethyl polysaccharide without further substitution, such as carboxymethyl cellulose, preferably having a degree of substitution of 0.3-3.0, more preferably 0.5-1.5. For such carboxymethylated polysaccharides, the process advantageously comprises the further step of contacting the crosslinked polysaccharide with an organic solvent which is at least partly miscible with water, between step (b) and step (c).

The organic solvent is preferably a water-miscible alcohol such as methanol, ethanol, methoxyethanol or isopropanol, a water-miscible ether such as dioxane, tetrahydrofuran or dimethoxyethane, or a water-miscible ketone, such as acetone. Most preferred are methanol and ethanol. The amount of solvent can be e.g. 2-30 times the amount of the gelled polysaccharide. The water-miscible solvent is evaporated before or during step (d).

[0010] The carboxymethylated polysaccharide can also be a carboxymethyl polysaccharide containing further carboxyl groups produced by oxidation of saccharide carbinol groups. Such carboxyl groups may be 2- and/or 3-carboxyl groups obtained by oxidation of anhydroglycose rings of the polysaccharide using hypochlorite or periodate/chlorite, but preferably they are 6-carboxyl groups obtained by oxidation of the 6-hydroxymethyl group, e.g. with a nitroxyl compound (TEMPO) as a catalyst. In such carboxy-carboxymethyl polysaccharide, such as 6-carboxy-carboxymethyl starch or 6-carboxy-carboxymethyl-cellulose, the degree of substitution for carboxymethyl is preferably 0.2-0.8, especially 0.3-0.6, and the degree of substitution for (6-carboxyl groups is preferably 0.1-0.5, more preferably 0.15-0.4.

[0011] Suitable oxidation methods are described in WO 98/27117 and references cited therein. TEMPO oxidation may be performed with hypochlorite with or without bromide as a catalyst, or with peracid/bromide or another oxidant. Unsubstituted TEMPO or 4-hydroxy or 4-acetamido-TEMPO or mixtures thereof may be used. When oxidations resulting in salt production are used, the salts may advantageously be removed after the oxidation reaction.

[0012] Similarly, the acidic polysaccharide may contain both other acidic groups obtained by substitution, and carboxyl groups obtained by oxidation. Such other acidic groups obtained by oxidation include e.g. phosphonic groups obtained by phosphorylation of the polysaccharide, sulphonyl groups and carboxyalkylcarbonyl groups obtained by reaction with a dicarboxylic anhydride. Substitution and oxidation may be performed in either order, e.g. first phosphorylation and then oxidation, or first oxidation and then phosphorylation. Combinations of different acidic substituents e.g. carboxyalkyl groups and phosphonic groups are also suitable.

[0013] In such oxidised and substituted (carboxyalkyl or other) polysaccharides the addition of an organic water-miscible solvent can be dispensed with, as a gel with the required structure already results from direct cross-linking.

[0014] The polysaccharide containing acidic groups can also be a carboxylated polysaccharide wherein the carboxyl groups have been introduced by oxidation of saccharide carbinol groups in a manner as described above, without carboxyalkylation. Such oxidised polysaccharides include dicarboxy polysaccharides (obtained by C2-C3 oxidation) and,

especially 6-carboxy polysaccharides, e.g. obtained by TEMPO oxidation, especially 6-carboxy starch. These polysaccharides do not require the use of a water-miscible solvent after crosslinking.

[0015] The polysaccharide containing acidic groups may also be a mixture of acidic polysaccharides as described above. A particularly useful mixture is a mixture of carboxymethyl cellulose and 6-carboxy starch, e.g. in a ratio of between 1:1 and 1:20. Other mixtures are also quite useful, e.g. carboxymethyl cellulose and carboxymethyl starch, or carboxymethyl starch and cellulose phosphate having a degree of substitution of about 0.3 to about 0.5.

[0016] The polysaccharide containing acidic groups is reacted with a crosslinking agent to produce a gel. A gel is defined herein as a polymeric network based on polysaccharides, which swells in water and does not dissolve in water. Crosslinking agents are reagents containing two or more functions capable of reacting with a hydroxyl group, resulting in intra- and inter-molecular bonds between different mono-saccharide units. Suitable crosslinking agents may act on the hydroxyl groups of different polysaccharide chains and include divinyl sulphone, epichlorohydrin, diepoxybutane, diglycidyl ethers, diisocyanates, cyanuric chloride, trimetaphosphates, phosphoryl chloride, and mixed anhydrides, and also inorganic crosslinkers such as aluminium and zirconium ions, but are not restricted to these examples. Mixtures of crosslinkers may also be used.

[0017] Especially preferred crosslinkers, in particular for crosslinking at elevated temperature and/or concentration, are crosslinkers that are active under neutral or acidic conditions, such as bis-epoxy crosslinkers, for example diepoxybutane, 1,5-diepoxyhexane, 1,7-diepoxyoctane, bis-glycidyl ether, glycol bis-glycidyl ether, butanediol bis-glycidyl ether and the like, as well as mixtures of different crosslinkers. Crosslinking can also be performed using carboxyl or aldehyde groups formed by oxidation or carboxyl groups introduced by carboxyalkylation, e.g. using polyols, polyamines or other polyfunctional reagents. Esterification and other crosslinking methods described herein can also be effected intramolecularly at the surface between the carboxyl group of one polysaccharide chain and a hydroxyl group of another chain as known in the art. This inter-chain crosslinking can be catalysed by an acid or a multivalent ion such as magnesium or calcium, or by heating. Divinyl sulphone is another preferred crosslinker. Crosslinking of starch and other polysaccharides is well-known in the art. A description of crosslinking agents and reaction conditions can be found e.g. in *"Starch Derivatives: Production and Uses"* by M.W. Rutenberg and D. Solarek, Acad. Press Inc., 1984, pages 324-332.

[0018] According to a preferred embodiment of the invention, crosslinking is performed

under conditions of increased temperatures and high concentrations. The temperatures are typically at least 100°C, more preferably between 120 and 180°C. The concentration of the polysaccharide to be crosslinked is at least 20 % by weight, more particularly between 25 and 65 % by weight with respect to the total aqueous crosslinking mixture. The crosslinking mixture may further contain a plasticiser such as a polyol. Suitable polyol plasticisers include glycerol, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, glycol and glycerol monoesters, sorbitol, mannitol, monosaccharides, citric acid monoesters and the like. The amount of plasticiser may vary from 1 to 25 % weight of the crosslinking mixture. The crosslinking can be conveniently performed in a kneading apparatus or an extruder under conditions of reactive processing. The various components of the crosslinking mixture can be mixed before entering the extruder, or one or more of them, e.g. the crosslinking agent, may be added at a later stage in the extruder.

[0019] After crosslinking, the crosslinked polysaccharide is treated with an acid so as to reduce the pH to 3.5 to 5.5. However, if the crosslinking is performed under acidic conditions, such as with bis-epoxy crosslinkers, the acidification takes place before crosslinking, and an adjustment of a pH to between 3.5 and 5.5 may or may not be needed after the crosslinking step. Suitable acidifying reagents include inorganic and organic acids such as hydrochloric, phosphoric, acetic acid etc. If crosslinking is performed under normal conditions (ambient temperature or up to about 100°C, atmospheric pressure, lower concentration) or before acidification, it is preferred that the polysaccharide is acidified to pH 4.9 or lower. After acidification, the cross-linked, gel-like material is comminuted to smaller particles, e.g. in the range of 0.5-5 mm.

[0020] Instead of or in addition to the treatment with the water-miscible organic solvent described above, an additional post-crosslinking step (surface crosslinking) may be applied to strengthen the gel. This post-crosslinking may be performed after the comminuting step c or even after the drying step d, resulting in different swelling degrees of the gel particles obtained. The crosslinking agent to be used in this post-crosslinking step can be the same as those referred to above for the first crosslinking step. In this procedure, the gel particles are slightly swollen, and treated and mixed with a crosslinking agent, and subsequently the particles are dried at a temperature which depends on the liquid used to swell the gel particles and on the crosslinking agent. The post-crosslinking may be performed in the presence of compounds providing further crosslinks at the outside of the gel particle. Such compounds may include bifunctional or multifunctional capable of reacting with hydroxyl and (if still present) carboxyl functions, for example diamines, polyamines, polyamide-

amine-epichlorohydrin (PAE resin), bis-epoxy compounds, chitosan-like compounds, metal salts (zirconium, aluminium), dialdehydes, or polyaldehyde-polycarboxy starch derivatives.

[0021] The comminuted material is dried, preferably in a fluidised bed drier. Drying can be performed at ambient temperatures, but preferably increased temperatures are used, in particular above 50°C, more in particular above 70°C. Drying times from 15 minutes up to 8 hours or more can be applied. Preferably an additional heat treatment is performed after the initial (fluidised bed) drying; this additional drying step can be performed at 80-150°C e.g. for 2 minutes to 2 hours, and results in a further enhanced gel strength of the product.

[0022] The invention also pertains to a bacteriologically stable superabsorbent polysaccharide derivative having odour control of absorbed liquid, as well as to a superabsorbent article in which this derivative is incorporated. The derivative and the article preferably have a pH below 5 (down to 3.5) when contacted with neutral or near-neutral water; if necessary, an acidifying agent can be incorporated in a sufficient amount to maintain the required low pH. Suitable acidifying agents include organic di- or poly-carboxylic acids such as citric, maleic, fumaric, oxalic, malonic, succinic, tartaric and similar acids, hydroxyacids such as gluconic, ascorbic, glycolic, glyceric, lactic, malic, salicylic acid and the like, as well as benzoic acid and phosphoric and other inorganic acids. These acids may be used in combination with their partially neutralised salts (e.g. monosodium citrate or monopotassium phosphate) to provide buffering capacity. Also, neutral materials such as acid anhydrides and lactones, e.g. maleic anhydride, succinic anhydride, δ -gluconolactone, can be incorporated for lowering the pH.

[0023] The superabsorbent polysaccharides combine high absorption capacity with control of bacterial growth and control of odour, as well as with biodegradability. The absorption capacity can be expressed as free swelling capacity (FSC) and the centrifugal retention capacity (CRC), and with the absorption under load (AUL), using synthetic urine (SU) as test liquid. The composition of the synthetic urine is as follows: 300 mM urea, 60 mM KCl, 130 mM NaCl, 2.0 mM $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 3.5 mM MgSO_4 , and 1 mg/l Triton X-100 in deionised water.

[0024] The superabsorbent polysaccharide derivatives of the invention can be used for absorbing liquids, especially of body fluids which contain various salts and non-ionic substances. The product is particularly suitable for the production of absorbent hygiene articles, such as diapers, sanitary napkins and the like. Such articles can be produced entirely on the basis of the polysaccharides according to the invention, but they can also contain conventional absorbent materials, such as cellulose pulp in addition to the absorbents

according to the invention. The absorbent article is preferably part of a layered product, in which the superabsorbent polymer constitutes at least one layer. The absorbent layer can be located between a liquid-pervious top layer and a liquid-impervious bottom layer. In particular the product may have four layers. The first one can be a thin, non-woven layer of polyester fibres or other fibres. The second layer can be a wadding which is used for acquiring and spreading the absorbed fluid such as urine. The third layer can consist of fluff pulp wherein the SAP is spread as fine particles, especially 50-800 μm . The last layer can be a back sheet of a water-resistant material such as polyethylene, which prevents leakage from the layered absorption product.

Example 1: Absorbent 6-carboxy-carboxymethyl potato starch

[0025] Carboxymethyl starch (degree of substitution 0.5) derived from potato starch was converted to 6-carboxy carboxymethyl starch by TEMPO-catalysed oxidation (degree of oxidation 0.25). A 20% aqueous solution of the product was cross-linked with different amounts of divinyl sulphone (0.5, 0.6, 0.7 mol% DVS). After 15 hours, an insoluble network was formed. The gel was brought into distilled water and allowed to swell. The pH of the material was lowered to pH 4.1 by controlled addition of 1M HCl. After equilibration, the gel was filtrated and dried in a fluidised bed drier at 70°C. The following absorption characteristics (FSC, CRC, AUL at 2.0 kPa) measured in synthetic urine (SU) were obtained:

Cross-linking degree (mol% DVS)	FSC (g/g)	CRC (g/g)	AUL (g/g) 2 kPa	pH gel
0.5	31	19	12	4.1
0.6	30	18	14	4.1
0.7	27.5	17	18.5	4.1

Example 2: Absorbent 6-carboxy-carboxymethyl high amylose corn starch

[0026] Carboxymethyl starch (degree of substitution 0.53) derived from high amylose corn starch was converted to 6-carboxy carboxymethyl starch by TEMPO-catalysed oxidation (degree of oxidation 0.09). A 20% aqueous solution of the product was cross-linked with different amounts of divinyl sulphone (1.0, 1.5, 2.0, 2.5 mol% DVS). After 16 hours, an insoluble network was formed. The gel was brought into distilled water and allowed to swell. The pH of the material was lowered to about pH 4.1 by controlled addition of 1M HCl. After equilibration, the gel was filtrated and dried in a fluidised bed drier at 80°C. The

above table summarises the absorption characteristics (FSC, CRC, AUL) measured in synthetic urine (SU) as obtained.

Cross-linking degree (mol% DVS)	FSC (g/g)	CRC (g/g)	AUL (g/g) 2 kPa	pH gel
1.0	29.5	20	17	4.0
1.5	34.5	20.5	13	4.1
2.0	33.0	18	16	4.3
2.5	28.5	16	17	4.0

5 **Example 3: Absorbent carboxymethyl cellulose treated with methanol**

DXL ¹	XL reaction ² cond. (°C/h)	FBD (°C/min)	FSC (g/g)	CRC (g/g)	AUL (g/g)
10	20°/20h ³	100°/10m	29	11	17
10	20°/20h	100°/10m	34	16	22
10	80°/3h	100°/10m	38	18	20
20	50°/8h	100°/10m	19.5	6.5	14
10	50°/8h	100°/10m	28.5	12	19.5
5	50°/8h	100°/10m	31.5	15	20.5
5	50°/15h	100°/15m	34.5	18	23
5	50°/15h	80°/15m	40	19.5	21
5	50°/15h	60°/15m	34	15.5	20
5	50°/15h	40°/30m	33	15	18.5

¹: degree of crosslinking used, (mol% BDDE)

²: crosslinking reaction

³: pH controlled by acetic acid instead of HCl.

10 **[0027]** A 2 wt.% aqueous solution of CMC (Cekol 50,000 from Metsa Specialty Chemicals, degree of substitution 0.8) was prepared and the pH was adjusted to 4.0 by slow addition of HCl under stirring (alternatively, glacial acetic acid can be used according to WO 86/00912, example 2b). The required amount of a 10 or 20 vol.% aqueous solution of 1,4-butanediol diglycidyl ether (BDDE) was added and the reaction mixture was thoroughly
15 mixed. The gel obtained was cut into pieces and suspended overnight in a fivefold excess of

methanol. The methanol was filtered out and the gel was milled in a blender, and the particles were dried in a fluidised bed drier (FBD). The dried product was ground in a mortar. The absorption characteristics for synthetic urine (SU) are summarised in the table above, with details on crosslinking and drying.

Example 4: Absorbent carboxymethyl cellulose treated with methanol

[0028] A 2 wt.% solution of CMC (Cekol 50,000 from Metsa Specialty Chemicals, degree of substitution 0.8) in 0.05 M aqueous NaOH was reacted with 14 mol% of DVS for 18 hours at room temperature. The gel obtained was chopped in pieces of roughly 3-4 cm and the pieces were brought in a fivefold excess of methanol. The gel was then acidified using 1M HCl to a pH varying from 4.4 to 4.0. After about 24 h the swollen gel was milled in a blender to obtain smaller particles, and then put back in the methanol for another 24 h to achieve homogeneous acidification of the gel material. Thereafter ground particles were dried in a fluidised bed drier at 100°C for 30 min, and then further heat-treated at 120°C in an oven for about 30 min. The absorption characteristics for SU are summarised in the following table.

amount of acid added (ml)	pH gel	before thermal treatment			After thermal treatment		
		FSC (g/g)	CRC (g/g)	AUL (g/g)	FSC (g/g)	CRC (g/g)	AUL (g/g)
28	4.4	83	64	10	40	26	17
30	4.2	57	42	12	29	17	16.5
33	4.0	55	41	13	28	15	16
35	4.0	39	26	13	21	11	15

Example 5: Absorbent carboxymethyl cellulose treated with ethanol

[0029] Ten grams of CMC (Cekol 50,000) were dissolved in 500 ml NaOH (0.05 mol/l). At room temperature 0.62 ml DVS (14 mol%) was added under stirring. After 18 hours the crosslinked gel (450 g) was chopped into pieces and 28 ml of 1 mol/l HCl was added and thoroughly mixed to decrease the pH of the gel to 4.4. After 1 h 1400 ml of ethanol was added. After one week, the precipitated gel was ground with a blender and dried in an FBD for 30 minutes at 100°C. The dry particles were milled and sieved to obtain a final particle size of 100-800 µm. The following absorption characteristics (FSC, CRC, AUL) measured in synthetic urine were obtained: FSC: 132 g/g; CRC: 111 g/g; AUL: 11 g/g; pH gel 4.4.

Example 5a: Absorbent carboxymethyl cellulose treated with ethanol

[0030] In addition to the sample of example 5, a heat treatment was applied for 30 minutes at 120°C in an oven to improve the gel strength (AUL). The following absorption characteristics measured in synthetic urine were obtained: FSC: 52 g/g; CRC: 37 g/g; AUL: 17 g/g; pH gel 4.5.

Example 6: Absorbent carboxymethyl cellulose treated with ethanol

[0031] Ten grams of CMC (Cekol 50,000, DS 0.8) were dissolved in 500 ml water and 8.5 ml 1 mol/l HCl (pH 4.4). Then 1.27 ml of 20 % (v/v) BDDE in water (3 mol%) was added with stirring. After 8 hours at 50°C, the crosslinked gel was suspended in a threefold volume of ethanol with stirring. After one week, the precipitated gel was ground into small pieces with a blender and dried in a FBD for 15 minutes at 100°C. The dry particles were milled and sieved to obtain a final particle size of 100-800 µm. The following absorption characteristics measured in synthetic urine were obtained: FSC: 21 g/g; CRC: 13 g/g; AUL: 18 g/g; pH gel 4.3.

Example 7: Absorbent 6-carboxy starch/CMC crosslinked under alkaline conditions

[0032] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) and 0.4 g of CMC (Cekol 50,000 from Metsa Specialty Chemicals, degree of substitution 0.8) were dissolved in 20 ml of 0.05 M aqueous NaOH (pH 12) under mechanical stirring for 4 h. The mixture was crosslinked with 0.8 mol% of DVS (23 µl) at 5°C for 18 hours. Three g of the gel obtained was chopped in pieces and the pieces were brought in 600 ml of demi water and acidified with 1.8 ml of 1M HCl with mild stirring (stepwise addition of acid). The next day, the swollen gel was filtered over a 80 µm sieve, and brought in another 600 ml of demi water for half an hour. Subsequently the gel was dried in a fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 93% TOS / 7% CMC: FSC: 30 g/g, CRC: 17 g/g, AUL: 16.5 g/g, pH gel 4.6.

Example 8: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions

[0033] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) and 0.4 g of CMC (Cekol 50,000 from Metsa Specialty Chemicals, degree of substitution 0.8) were dissolved in 20 ml of demi water under mechanical stirring for 1 h. The pH was adjusted to 4.5 using 25% HCl. The mixture was crosslinked with 1.4 mol% of BDDE (1,4-butanediol

diglycidyl ether) (78 μ l) at 50°C for 18 hours. The gel was chopped and the pieces were dried in a fluidised bed drier for 30 minutes at 100°C. The dried gel was ground and washed with excess demi water on a 80 μ m sieve to remove any salts present. Then the gel was dried in the fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 93% TOS / 7% CMC: FSC: 26 g/g, CRC: 15.5 g/g, AUL: 19 g/g, pH gel 4.9.

Example 9: Absorbent 6-carboxy starch crosslinked under acidic conditions

[0034] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) was dissolved in 20 ml of demi water under mechanical stirring for 1 h. The pH was adjusted to 4.5 using 25% HCl. The mixture was crosslinked with 2.0 mol% of BDDE (113 μ l) at 50°C for 18 hours. The gel was chopped and the pieces were dried in a fluidised bed drier for 30 minutes at 100°C. The dried gel was ground and washed with excess demi water on a 80 μ m sieve to remove any salts present. Then the gel was dried in the fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 100% TOS: FSC: 27 g/g, CRC: 16 g/g, AUL: 19 g/g, pH gel 4.8.

Example 10: Crosslinking of 6-carboxy starch by extrusion

[0035] In an extruder, 50 grams of 6-carboxy starch (0.25 mol) is mixed with 50 ml of a 0.3 M HCl solution containing 30 μ l butanediol diglycidyl ether (0.15 mmol). The paste is then extruded at 150°C with an average residence time of 1 minute in the extruder. At the extrusion die the crosslinked polysaccharide is chopped into small pieces. The small pieces of gel are then dried in a fluidised bed drier for 30 minutes at 100°C. The dried particles are ground and sieved to obtain a final particle size of 100-800 μ m. The absorption properties are comparable to those of the superabsorbent polysaccharide crosslinked in a conventional way.

Example 11: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions.

[0036] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 20wt%, 40wt% and 50wt% TOS solutions, respectively. The pH of the solutions was about 4.6. To the solutions 0.124 g of CMC (Cekol 50,000, degree of substitution 0.8) was added, followed by thorough mixing. The mixtures were crosslinked at 50 °C for 18 hours, with 1.4, 0.7, and 0.5 mol% of BDDE, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed

drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 µm sieve to remove salts present. Then the gels were dried in the fluidised bed drier at 100 °C for 1 hour. The materials were characterised in synthetic urine with the following results for the 40% TOS material: DXL (= degree of crosslinking in mol% BDDE): 0.7; FSC: 26.5 g/g; CRC: 15.5 g/g; AUL 14 g/g; pH gel: 4.2. Comparable results were obtained when using 20% or 50% TOS solutions, instead of 40%.

Example 12: Absorbent 6-carboxy starch crosslinked under acidic conditions.

[0037] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 20wt%, 40wt% and 50wt% TOS solutions, respectively. The pH of the solutions was about 4.6. The solutions were cross-linked at 50 °C for 18 hours, with 2.0, 0.75, and 0.6 mol% of BDDE, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 µm sieve to remove salts present. Then the gels were dried in the fluidised bed drier at 100 °C for 1 hour. The materials were characterised in synthetic urine with the following results for the 40% TOS material: DXL 0.75; FSC: 28 g/g; CRC: 15 g/g; AUL 14 g/g; pH gel: 4.1. Comparable results were obtained when using 20% or 50% TOS solutions instead of 40%.

Example 13: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions

[0038] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 40wt% TOS-solutions. The pH of solutions was about 4.6. To each solution 0.124 g of CMC (Cekol 50,000, degree of substitution 0.8) was added, and the whole was mixed thoroughly. Mixtures were cross-linked with 0.7 mol% of BDDE at 50 °C for 18 hours, 70 °C for 2.5 hours, and 100 °C for 1 hour, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 µm sieve to remove any salts present. Then the gels were dried in the fluidised bed drier at

100 °C for 1 hour. The materials were characterised in synthetic urine with the following results:

5	XL temp. (°C)	XL time (h)	FSC (g/g)	CRC (g/g)	AUL (g/g)	pH gel
	50	18	26.5	15.5	14	4.2
	70	2.5	27	14	13	3.8
10	100	1	27	15.5	11.5	3.9

Example 14: Absorbent 6-carboxy starch crosslinked under acidic conditions.

[0039] Fifty g of desalted freeze-dried TEMPO-oxidised starch (TOS, degree of oxidation 0.70) was kneaded till a fibrous structure was obtained, and subsequently demi
15 water (21.4 ml of demi water) was added. The whole was kneaded for 3 minutes at 17 °C to obtain 70 wt% TOS paste (pH of paste was ca. 4.6). To this paste 0.4 mol% BDDE was added and the whole was again kneaded for 3.5 minutes at 17 °C. Then the paste was crosslinked for 16 hours at 50 °C. The gel obtained was sized and dried in a fluidised bed drier for 1 hour at 80 °C. Dried gel particles were re-swollen in 10 liters of demi water,
20 and subsequently dried in the fluidised bed drier for 1.5 hours at 80 °C. The material was characterised in synthetic urine with the following results: FSC: 27 g/g, CRC: 14.5 g/g, AUL: 17.5 g/g, pH gel 4.9.

Claims

1. A process of producing a superabsorbent polysaccharide derivative, comprising the steps of:
 - (a) crosslinking at least one polysaccharide containing acidic groups with a crosslinking agent to produce a gel;
 - (b) ensuring that the pH of the polysaccharide is between 3.5 and 5.5;
 - (c) comminuting the acidified polysaccharide gel; and
 - (d) drying the comminuted polysaccharide at elevated temperature.
2. A process according to claim 1, in which the polysaccharide containing acidic groups comprises carboxymethyl-cellulose, further comprising the step of contacting the crosslinked polysaccharide with an organic solvent which is at least partly miscible with water, between step (b) and step (c).
3. A process according to claim 2, in which said organic solvent is a lower alcohol, a water-miscible ketone or a water-miscible ether, especially methanol or ethanol.
4. A process according to claim 1, in which the polysaccharide containing acidic groups is a carboxymethyl polysaccharide further containing carboxyl groups resulting from oxidation of saccharidic hydroxymethyl or hydroxymethylene groups, or phosphonic or sulphonic acid groups.
5. A process according to claim 1, in which the polysaccharide containing acidic groups comprises a 6-carboxy polysaccharide, especially 6-carboxy starch, optionally mixed with a carboxyalkylated polysaccharide.
6. A process according to any one of claims 1-5, in which the polysaccharide containing acidic groups contains 0.3-3.0 carboxyl groups per monosaccharide unit.
7. A process according to any one of claims 1-6, in which said cross-linking agent is a bis-epoxy compound, and the polysaccharide is acidified before step (a).

8. A process according to any one of claims 1-7, in which said crosslinking step is performed at a temperature of at least 100°C, preferably between 120 and 180 °C and/or at a concentration of the polysaccharide of between 25 and 75% by weight.
9. A process according to claim 8, in which a plasticiser such as glycerol is used during said crosslinking step.
10. A process according to any one of the preceding claims, in which said drying step (d) is performed using a fluidised bed, at a temperature of between 50 and 130°C.
11. A process according to any one of the preceding claims, in which said drying step (d) is followed by a heat treatment at a temperature of between 80 and 150°C.
12. A process according to any one of the preceding claims, in which an additional surface-crosslinking step is performed after step (c) or after step (d).
13. Superabsorbent polysaccharide derivative obtainable by the process according to any one of the preceding claims, and having a pH below 5.
14. Superabsorbent polysaccharide according to claim 13, also comprising an acid selected from organic di- and polycarboxylic acids, hydroxycarboxylic acids and benzoic acids.
15. Absorbent article comprising a superabsorbent polysaccharide according to claim 13 or 14.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NL 99/00776

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L15/60 A61L15/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 2, line 9-15 - line 53-57 page 3, line 3,4 - line 19,20 page 3, line 55-58 claim 1 ----- -/-	1-7, 11, 13-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 April 2000

Date of mailing of the international search report

20/04/2000

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 99/00776

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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PATENT COOPERATION TREATY

From the
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2-6-01

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

16-6-01

Date of mailing
(day/month/year) 02.05.2001

Applicant's or agent's file reference
BO 42290

IMPORTANT NOTIFICATION

International application No.
PCT/NL99/00776

International filing date (day/month/year)
16/12/1999

Priority date (day/month/year)
16/12/1998

Applicant
SCA HYGIENE PRODUCTS ZEIST B.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BO 42290		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL99/00776	International filing date (day/month/year) 16/12/1999	Priority date (day/month/year) 16/12/1998	
International Patent Classification (IPC) or national classification and IPC A61L15/60			
Applicant SCA HYGIENE PRODUCTS ZEIST B.V. et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input checked="" type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 			
Date of submission of the demand 13/07/2000		Date of completion of this report 02.05.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-90298 Munich Tel: +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Heller, D Telephone No. +49 89 2399 8746	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL99/00776

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-13 as originally filed

Claims, No.:

1-15 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

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(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	8-12
	No	Claims	1-7, 13-15
Inventive step (IS)	Yes:	Claims	
	No	Claims	1-15
Industrial applicability (IA)	Yes:	Claims	1-15
	No	Claims	

2. Citations and explanations
see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

SECTION V:

Subject-matter

Independent present claim 1 is directed to a process of producing a superabsorbent polysaccharide derivative, comprising the steps of:

- a) crosslinking at least one polysaccharide containing acidic groups with a crosslinking agent to produce a gel;
- b) ensuring that the pH of the polysaccharide is between 3.5 and 5.5;
- c) comminuting the acidified polysaccharide gel; and
- d) drying the comminuted polysaccharide at elevated temperature.**

Independent claim 13 relates to a derivative obtainable by the claimed process and independent claim 15 discloses an absorbent article comprising the derivative of claim 13.

Prior art

Reference is made to the following documents:

- D1: (EP-A-0 644 207) provides a superabsorbent polymer preparable by the process of first providing a solution containing carboxylic acid monomers or water soluble salts thereof, and a crosslinking agent. The carbonated monomer solution is then polymerized at temperatures ranging from about 0°C to about 130°C, forming a microcellular hydrogel. The microcellular hydrogel is chopped or ground into gel pieces having a particle diameter ranging from about 0.1 mm to about 5.0 cm. The gel pieces are dried at temperatures ranging from about 85°C to about 210°C, and are then ground to form a polymer having a particle size of from about 0.05 mm to about 5.0 mm (p. 3, ll. 13 to 18).
- D2: (WO 98 27117 A; cited in the application) relates to a superabsorbent material based on polysaccharides and to a method of producing such material (p. 1, ll. 2 to 4).
- D4: (US-A-5 371 208) provides electrophoresis gels giving improved resolution of small biomolecules, electrophoresis gels of such a low polymer concentration that

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separated bands in the gel are not bent (col. 8, ll. 48 to 54).

- D5: (US-A-4 582 865) provides highly swollen gels of cross-linked hyaluronic acid (col. 1, ll. 37 and 38).
- D6: (EP-A-0 530 438) is directed to superabsorbent polymers, i.e., hydrogel forming polymers. (p. 1, ll. 41 to 43).
- D7: (EP-A-0 083 267) relates to a method of preparing inocula of low water activity having a long storage life and improved resistance to temperature and rehydration, according to which microorganisms of the genus *Rhizobium* in a culture medium containing a carbohydrate source are incorporated in a polymer gel and the water activity of the resulting inoculum is then lowered to and maintained at less than 0.1. (p. 5, ll. 4 to 7).
- D8: (Coviello T. et al, J Controlled Release, vol. 55, no. 1, 1998, page 57-66) is directed co-crosslinked polysaccharide and discloses studies for a controlled delivery matrix (title).

Novelty

The subject-matter of claims 1 to 11, 13 to 15 is not new in the sense of Article 33 (2) PCT.

Due to its content as described above, D1 anticipates novelty of present claims 1 (p. 1, ll. 13 to 18), 2 and 3 (p. 4, ll. 49 to 54), 4 (p. 1, ll. 13 to 18), 8 (p. 1, ll. 13 to 18), 9 (example 2), 10 and 11 (claim 1), 13 and 14 (p. 1, ll. 13 to 18), 15 (p. 7, ll. 11 to 13).

D2 contains all the essential features including step (b) of adjusting the pH of 5 (see example 1). Therefore, present claims 1 to 3 (p. 5, ll. 16 to 30 and p. 2, ll. 21 to 23), 4 and 5 (p. 3, ll. 5 to 21), 6 (p. 3, l. 28), 7 (p. 5, ll. 16 to 30), 13 and 14, 15 (p. 6, ll. 10 to 16) are not novel over D2.

D6 anticipates novelty of present claims 13 to 15 (p. 4, l. 54). As D6 does not contain step (b) of adjusting the pH, it does not anticipate novelty of present claims 1 to 12.

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The same as for D6 applies for D7 (p. 5, l. 31 to p. 6, l. 23).

D8 lacks only the drying step at elevated temperatures (see p. 59, right col. §2). Therefore, present claims 1 to 12 are novel over D8. But D8 contains the same product disclosed in present claims 13 and 14 (see p. 59, "2.2. Preparation of the co-crosslinked polymer"). Therefore, said claims are not novel over D8. Claim 15 is not novel (abstract, ll. 4 to 6).

- D1 does not affect novelty of present claims 1 to 15, because D1 discloses superabsorbent acrylate polymers and not polysaccharides as claimed in the present application.

It seems that D4 does not anticipate novelty of present claims 1 to 15, because D4 discloses a crosslinking reaction performed at a basic pH (col. 1, ll. 32 to 34). The other features of claim 1 are disclosed in D4 (col. 11, l. 4; col. 11, l. 48 to col. 12, l. 13).

D5 lacks the drying step and uses the gel for cosmetical and medical formulations (col. 4). Therefore, present claims 1 to 15 are novel over D5.

The subject-matter of claims 8 to 12 is new in the sense of Article 33 (2) PCT.

Inventive step

The subject-matter of claims 8 to 12 does not involve an inventive step in the sense of Article 33 (3) PCT.

The additional features of claims 8 to 12 can be determined as alternatives which can be derived from D1 for example and are therefore not inventive in the sense of Article 33 (3) PCT.

SECTION VI:

The applicant is informed that no check has been made as to whether priority has been validly claimed. Therefore, document D3 (EP-A-0 889 063), which has been

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disregarded in writing the present opinion, could become relevant for the assessment of novelty once the present application enters the regional phase (Rule 64 (1) b PCT).